Kinetic studies on the degradation of crystal violet by the Fenton oxidation process
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ABSTRACT
The degradation of dye crystal violet (CV) by Fenton oxidation process was investigated. The UV–Vis spectrogram has shown that CV can be degraded effectively by Fenton oxidation process. Different system variables namely initial H$_2$O$_2$ concentration, initial Fe$^{2+}$ concentration and reaction temperature, which have effect on the degradation of CV by Fenton oxidation process, have been studied systematically. The degradation kinetics of CV was also elucidated based on the experimental data. The degradation of CV obeys the first-order reaction kinetics. The kinetic model can be described as $k = 1.5 \exp(-7.5/n)(RT)$[$[H_2O_2]^{0.8718}[Fe^{2+}]^{0.5062}$]. According to the IR spectrogram, it is concluded that the benzene ring of crystal violet has been destroyed by Fenton oxidation. The result will be useful in treating dyeing wastewater containing CV by Fenton oxidation process.

Key words | crystal violet, Fenton, hydroxyl radical, kinetic

INTRODUCTION
Dye pollutants from textile dyeing and printing industries are major sources of water contamination. The effluents discharged from these industries are usually strongly colored. Disposal of this colored water into receiving waters can cause damage to aquatic life by stopping the reoxygenation capacity of water and also blocking sunlight, thereby disturbing the natural growth activity of aquatic organisms (Wang 2008). It also causes severe damage to human beings due to their mutagenic and carcinogenic effects (Sivaraj et al. 2001; Kadirvelu et al. 2002; Mall et al. 2005). There are various methods used to remove dyes from aqueous solution such as activated carbon adsorption process, ozonation and anaerobic bioremediation (Robinson et al. 2001; Neamtu et al. 2004).

Recently, advanced oxidation processes (AOPs), which are based on the generation of highly reactive hydroxyl radicals as primary oxidant, has been developed (Andreozzi et al. 1999). AOPs appear as an attractive option for water treatment, particularly in cases where the contaminants are otherwise difficult to remove. Among these processes, the oxidation using Fenton oxidation process has proven to be a promising treatment method because of its high oxidation power, rapid oxidation kinetics, relatively cheap and easily operated and maintained (Sun et al. 2007a,b).

The Fenton oxidation process is a homogeneous catalytic oxidation method using a mixture of hydrogen peroxide (H$_2$O$_2$) and ferrous ions (Fe$^{2+}$) in acidic medium, which was not applied as an oxidizing process to destroy toxic organics until the late 1960s (Huang et al. 1993). It is known to be very effective in the removal of many hazardous organic pollutants from water. The main advantage is the complete destruction of contaminants to harmless compounds (Legrini et al. 1993). The mechanism that describe Fenton reaction principally includes the following reactions (Neyens & Baeyens 2003):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^-$$ (1)

The ferrous ion (Fe$^{2+}$) initiates and catalyses the decomposition of H$_2$O$_2$, resulting in the generation of
hydroxyl radicals (OH\(^{-}\)). The hydroxyl radicals, which is the second strongest oxidant (\(E^0 = 2.78\) V), only inferior to fluoride (\(E^0 = 3.06\) V), can rapidly and non-selectively react with a wide range of organic pollutants to mineralize them to \(\text{CO}_2\), \(\text{H}_2\text{O}\) and inorganic products (Guedes et al. 2003; Sun et al. 2009).

Ferrous ions are slowly regenerated between newly formed ferric ions and hydrogen peroxide. The reactions are shown as below (Neyens & Baeyens 2003):

\[
\begin{align*}
\text{Fe}^3^+ + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^-\text{OOH}^2^+ + \text{H}^+ \quad (2) \\
\text{Fe}^-\text{OOH}^2^+ & \rightarrow \text{HO}_2^- + \text{Fe}^{2+} \quad (3) \\
\text{Fe}^3^+ + \text{HO}_2^- & \rightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+ \quad (4)
\end{align*}
\]

Consequently, the oxidation rate of organic compounds is fast when large amount of ferrous ions are present because large amount of hydroxyl radicals are produced. However, the Fenton reaction may slow down due to the slow ferrous ion production.

Nevertheless, numerous competitive reactions can also occur, which negatively affect the oxidation process (Neyens & Baeyens 2003):

\[
\begin{align*}
\text{OH}^- + \text{Fe}^{2+} & \rightarrow \text{OH}_2^- + \text{Fe}^{3+} \quad (5) \\
\text{OH}^- + \text{H}_2\text{O}_2 & \rightarrow \text{H}_2\text{O} + \text{HO}_2^- \quad (6)
\end{align*}
\]

Previous researches have shown that a number of dyes could be effectively degraded by Fenton oxidation process (Swaminathan et al. 2003; Ashraf et al. 2006; Behnajady et al. 2007; Sun et al. 2007a,b). And the degradation efficiency of dyes was mainly depended on their chemical characteristics, the generation rate and concentration of \(\text{OH}^-\) in the process.

In this study, research was carried out to investigate the degradation of a dye named crystal violet (CV) by Fenton oxidation process. Evidences based on UV–Vis spectrum and IR spectrum suggest that CV can be treated using Fenton reactions. The removal rate of CV and the kinetics were studied. The reaction parameters affecting the degradation such as initial concentration of \(\text{H}_2\text{O}_2\) and \(\text{Fe}^{2+}\), reaction temperature were studied. Furthermore, the degradation kinetics of CV was also established based on the experimental data. The results can provide fundamental knowledge for the treatment of dye wastewater containing CV by Fenton oxidation process.

**MATERIALS AND METHODS**

**Materials**

Crystal violet was obtained from Tianjin Tianxin Chemical Co. (Tianjin, China). Figure 1 shows the chemical structure of this dye. Hydrogen peroxide (50%, w/w) was obtained from Tianjin Bodi Chemical Co., LTD (Tianjin, China). Ferrous sulfate (\(\text{FeSO}_4\cdot 7\text{H}_2\text{O}\)) was obtained from Mianyang Chemical Co. (Xiantao, China). Sulfuric acid was obtained from Kaifeng Dongda Chemical Group Co., LTD. Reagent Factory (Kaifeng, China). All of the chemicals used were analytical grade without any further purification. Double distilled water was used throughout this study.

**Analytical methods**

To start each test, 1.0 mL \(1.2 \times 10^{-4}\) mol/L CV solutions was placed into a 25 mL colorimetric tube, then diluted to 12.5 mL with double distilled water and measured by UV–Vis spectrophotometer (Lambda 17, Perkin-Elmer Co., America) at 590 nm (\(\lambda_{\text{max}}, \text{the maximum absorbance wavelength}\)) with a spectrometric quartz cell (1 cm path length). This absorbance value was labeled as original absorbance of CV. The degradation kinetics of CV was also established based on the experimental data. The results can provide fundamental knowledge for the treatment of dye wastewater containing CV by Fenton oxidation process.

**Figure 1 | Chemical structure of CV.**
absorbance value $A_0$. $1.0 \text{ mL } 1.2 \times 10^{-4} \text{ mol/L CV solutions and } 1.0 \text{ mL } 2.0 \times 10^{-3} \text{ mol/L sulfuric acid solutions and appropriate volumes of hydrogen peroxide and ferrous sulfate solutions were placed into a 25 mL colorimetric tube, then diluted to 12.5 mL with double distilled water and analyzed by UV–Vis spectrophotometer. This absorbance value was marked as $A$, which is changed as a function of time. The reactions were timed when calculated amounts of hydrogen peroxide were added to the colorimetric tube. Therefore, removal rate ($a$) can be expressed as follow:

$$a = \frac{1 - A}{A_0}$$

Fourier Transform Infra-Red (FTIR) spectra were taken with a Spectrum One FTIR spectrophotometer (Perkin-Elmer Co., America) at room temperature.

**RESULTS AND DISCUSSION**

**UV–Vis spectra**

The UV–Vis spectrogram of CV at various reaction times is shown in Figure 2. The maximum absorbance wavelength ($\lambda_{\text{max}}$) of CV in the visible light region is 590 nm. The results showed that the absorption of the 590 nm absorption peaks decreased rapidly following the reaction beginning, and almost disappeared after 30 minutes. Therefore, it is concluded that CV can be degraded effectively by Fenton oxidation process.

**Effect of initial H$_2$O$_2$ concentration on the degradation of CV**

H$_2$O$_2$ plays a very important role as a source of OH$^-$ generation in Fenton reaction. The effect of initial H$_2$O$_2$ concentration on the degradation of CV was examined and the results were shown in Figure 3. From the figure, it can be observed that increasing the initial concentration of H$_2$O$_2$ from $6.4 \times 10^{-3}$ to $1.9 \times 10^{-2} \text{ mol/L}$ could enhance the removal rate of CV from 45% to 84% within 30 min of reaction. A rapid degradation of CV was observed in the first 10 min because of the hydroxyl radical resulting from the reactions between H$_2$O$_2$ and Fe$^{2+}$. 10 min after, there is a slower stage, due to the depletion of oxidants in the solution.

**Effect of initial Fe$^{2+}$ concentration on the degradation of CV**

Fe$^{2+}$ is another main parameter in Fenton’s reaction, which catalyzes the decomposition of H$_2$O$_2$ to generate OH$^-$. Figure 4 showed the effect of initial Fe$^{2+}$ concentration on the degradation of CV with different initial concentration. In the presence of increased the initial concentration of...
Fe$^{2+}$ from 2.4 x 10$^{-5}$ to 9.6 x 10$^{-5}$ mol/L, an improvement of the degradation of CV could be observed and the removal rate, achieved within 30 min of reaction, was enhanced from 57% to 87%. This phenomenon that higher removal rate achieved at high Fe$^{2+}$ concentration was mainly attributed to the higher production of OH$^-$ with more Fe$^{2+}$ in Fenton reaction.

Effect of temperature on the degradation of CV

The effect of temperature on the degradation of CV was studied at various temperatures of 25, 30, 35, 40, 50 °C, and the results were shown in Figure 5. As is shown from the Figure 5, raising the temperature has a positive impact on the degradation of CV. The removal rate within 10 min of reaction increased from 53.7% to 76.4% as an increasing the temperature from 25 to 50 °C. This can be explained that raising temperature could accelerate the generation rate of OH$^-$ and therefore enhance the degradation of CV.

Kinetics studies

The Fenton oxidation of CV can be represented by the following pth order reaction kinetics (Lin et al. 1999):

$$\frac{dC}{dt} = -kC^p$$  \hspace{1cm} (8)

where $C$ represents the CV concentration, $p$ the order of reaction, $k$ the kinetic rate constants and $t$ the time. For a first order reaction, the above equation becomes

$$\ln\left(\frac{C}{C_0}\right) = -kt$$  \hspace{1cm} (9)

in which $C_0$ is the initial CV concentration.

Because absorbance value is proportional to concentration, the Equation (9) can be changed as

$$\ln\left(\frac{A}{A_0}\right) = -kt$$  \hspace{1cm} (10)

Thus, a graph of ln$(A/A_0)$ to $t$ will yield a straight line with a slope of $k$.

The kinetic rate constants can also be represented by the following equation:

$$k = k_0[H_2O_2]^n[FeSO_4]^m_0$$  \hspace{1cm} (11)

in which [H$_2$O$_2$]$_0$ and [FeSO$_4$]$_0$ are the two initial concentrations in mol/L, $n$ and $m$ are the orders of concentration dependence. These two orders of concentration dependence can be obtained from the plots of ln$k$ versus [H$_2$O$_2$]$_0$ and [FeSO$_4$]$_0$ respectively as the slope.

The kinetic parameter in Equation (11), $k_0$, is related to the operating temperature by the following Arrhenius
equation:

\[ k_0 = A \exp\left( -\frac{E}{RT} \right) \]  

(12)

where \( A \) is frequency factor; \( E \) is the activation energy \((\text{J} \text{ mol}^{-1})\); \( R \) is the ideal gas constant \((8.314 \text{ J} \text{ mol}^{-1} \text{ K}^{-1})\).

Thus, the value of \( E \) and \( A \) can be obtained from the plot of \( \ln k \) versus \( 1/T \) as the slope and the intercept respectively.

Therefore, the kinetic model of degradation of CV by Fenton oxidation process can be described as

\[ k = A \exp\left( -\frac{E}{RT} \right) \frac{[\text{H}_2\text{O}_2]}{[\text{Fe}^{2+}]} \]  

(13)

The role of \( \text{H}_2\text{O}_2 \)

The effect of initial concentration of \( \text{H}_2\text{O}_2 \) on the kinetic rate constants for CV degradation was studied and the results are shown in Figure 6. It can be seen the CV degradation fits the first order kinetic model quite well under the given test conditions \((R > 0.9868)\). It also showed that the \( k \) of CV degradation as the slope increased with increasing \([\text{H}_2\text{O}_2]_0\) in the experiment conditions due to the increment of \( \text{OH}^- \) radical produced through the decomposition of increasing hydrogen peroxide. The relationship between the \( k \) of CV degradation and the initial \( \text{H}_2\text{O}_2 \) concentration was in a good linear and the linear regression equation is \( \ln[\text{H}_2\text{O}_2]_0 = 1.1554 + 0.8718 \ln k \), \( R = 0.9954 \). Therefore, the order of \( \text{H}_2\text{O}_2 \) concentration dependence is 0.8718.

The role of \( \text{Fe}^{2+} \)

The effect of \( \text{Fe}^{2+} \) concentration on the kinetic rate constants for CV degradation was studied and the results are presented in Figure 7. It can be seen the first order kinetic model is applicable to the CV degradation quite well under the given experiment conditions \((R > 0.9853)\). In addition, it can be observed that the values of \( k \) as the slope quickly increased when \( \text{Fe}^{2+} \) concentration increases from 2.4 to \( 6.4 \times 10^{-5} \text{ mol/L} \). However, the \( k \) of CV degradation was increased slowly when the initial \( \text{Fe}^{2+} \) concentration rose from \( 6.4 \) to \( 9.6 \times 10^{-5} \text{ mol/L} \). The phenomena could be explained that large excess of \( \text{Fe}^{2+} \) can react with some of the intermediates like \( \text{OH}^- \), due to the direct oxidation of the organic load (Pérez et al. 2002):

\[ \text{Fe}^{2+} + \text{OH}^- \rightarrow \text{Fe}^{3+} + \text{OH}_2^- \quad k = 3.0 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1} \]  

(14)

The relationship between the \( k \) of CV degradation and the initial \( \text{Fe}^{2+} \) concentration was in a good linear and the linear regression equation is \( \ln[\text{Fe}^{2+}]_0 = -1.0049 + 0.5062 \ln k \), \( R = 0.9955 \). Therefore, The order respective to \( \text{Fe}^{2+} \) concentration was 0.5062.
The role of temperature

The effect of temperature on the kinetic rate constants for CV degradation was studied. The results are shown in Figure 8 and indicate that the reaction is significantly affected by temperature. But it can be also concluded that the temperature has a little influence on the kinetic rate constants.

The Arrhenius plot of \( \ln k \) versus \( 1/T \) was a good linear relationship and the linear regression equation is

\[
\ln k = 0.4323 - 0.9003/T, \quad R = 0.9825.
\]

Thus, the activation energy \( E \) was found to be 7.5 KJ/mol, and \( A \) value was 1.5. Generally, the activation energy of ordinary thermal reactions is usually between 60 KJ/mol and 250 KJ/mol (Chen & Zhu 2007), the result implies that the degradation of CV by Fenton oxidation process requires lower activation energy and can be easily achieved.

Therefore, the kinetic model of the degradation of CV by Fenton oxidation can be described as:

\[
k = 1.5 \exp\left(\frac{-7.5}{RT}\right) \left[\text{H}_2\text{O}_2\right]_0^{0.8718} \left[\text{Fe}^{2+}\right]_0^{0.5062}
\]

IR spectra

The FTIR-spectra of CV and the deposition after reaction are shown in Figure 9. From the Figure 9(a), the absorption bands at 2519.31 and 2316.47 cm\(^{-1}\) can be assigned to \( \text{C} = \text{C} \) benzene ring. The absorption bands at 1583.10, 1521.75 and 1477.98 cm\(^{-1}\) can be attributed to \( \text{C} = \text{C} \) benzene ring. The absorption band at 1359.75 cm\(^{-1}\) can be related to \( \text{CH}_3 \). The absorption band at 1169.23 cm\(^{-1}\) can be characteristic of \( \text{C} = \text{N} \). The absorption bands at 939.97, 911.87, 828.35, 802.48 and 721.86 cm\(^{-1}\) can be attributed to out-of-plane bending of benzene ring. The absorption bands at 558.38 and 520.01 cm\(^{-1}\) can be related to \( \text{C} = \text{Cl} \).

Figure 9(b) has shown the IR spectrogram of the deposition after Fenton reaction. Compared with Figure 9(a), the percent of the main absorption wavelength apparently dimished and the absorption bands of benzene ring has disappeared. In the range of 2,700–3,379.33 cm\(^{-1}\), there would be a mixed broad band, which was possibly attributed to the stretching vibrations of \( \text{OH} \), \( \text{NH} \) and \( \text{C} = \text{H} \). The absorption band at 1635.90 cm\(^{-1}\) could be related to the stretching of \( \text{C} = \text{C} \) of chain hydrocarbon. The absorption band at 1,038.03 cm\(^{-1}\) would assigned to the stretching of \( \text{C} = \text{O} \), \( \text{C} = \text{C} \) bond. Thus, it can be deduced that OH-reacted with \( \text{N(CH}_3)_2 \) and benzene ring of CV to \( \text{NH} \) and \( \text{C} = \text{O} = \text{C} \), \( \text{C} = \text{C} \), respectively. Besides the deposition, the products also certainly have carbondioxide and water.

Therefore, it is concluded that the benzene ring has been destroyed by Fenton oxidation.

CONCLUSIONS

In this work, the degradation of CV by Fenton oxidation process has been studied. The UV–Vis spectrogram has shown that Fenton oxidation is an effective method for degradation of crystal violet. The test results showed that
the initial H₂O₂ concentration, the initial Fe²⁺ concentration and the temperature have affect on the reaction. Increasing the initial concentration of H₂O₂ and Fe²⁺ and the reaction temperature enhanced the removal rate of CV.

The kinetic study indicated that the degradation kinetics of CV followed the first-order kinetics well. The kinetic rate constants increased as advancing the initial concentration of H₂O₂ and Fe²⁺. But the temperature has a little influence on the kinetic rate constants. The reaction orders of H₂O₂ and Fe²⁺ concentrations dependence are 0.8718 and 0.5062, respectively. The activation energy E, for the degradation of CV by Fenton oxidation was determined to be 7.5 KJ/mol. The kinetic model also was established and can be described as:

\[ k = 1.5 \exp\left(-\frac{7.5}{RT}\right) [H_2O_2]^{0.8718} [Fe^{2+}]_0^{0.5062} \]

Comparing the IR spectrogram of CV with the deposition after reaction, it is educed that the benzene ring of crystal violet has been destroyed by Fenton oxidation.

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REFERENCES


